Preliminary tests of oils absorption by wool entrapped into alginate/Ca beads

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INTRODUCTION

Nowadays the purification of water from petroleum hydrocarbons is one of the most important problems across the world. The main problem may be caused by the fact that the standard treatment processes which are used to decontamination are limited in their application. First they are prohibitively expensive, and on the other hand they may be only partially effective. One from various scientific method that is useful in pollutant degradation, is bioremediation. During bioremediation in marine environment, nutrients, surfactants and microorganisms are used for purification of contaminated water from crude oil. However, dilution of these materials causes a lot of problems especially in open-water systems. A feasible solution of this problem might thus be seeding with immobilized microorganisms. Hence immobilization of cells onto macroalgae [Suzuki T. et al. 1998], chitin and chitosan flakes [Gentili A.R. et al. 2006], or inside of polyurethane foam [Oh Y.S. et al. 2000, Quek E. et al. 2006] or polystyrene surfaces [Ionata E. et al. 2005] could offer a higher surface area to facilitate growth of biomass and degradation rate. Additionally, it is also possible to use microorganisms immobilized in the microcapsules [Bogusławska-Wąs E. et al. 2005, Patil N.K. et al. 2006]. The encapsulation of cells in sodium alginate may also facilitate and increase degradation rate. The main problem of this process is that absorption of hydrocarbons by alginate capsules may be difficult. This is because of hydrophilic character of capsules. Therefore the solution of this problem can be addition of hydrocarbons absorbers into alginate capsules. Wool on one hand has very high hydrocarbons absorption capacity and furthermore properties besides it is natural and biodegradable material. This is the reason why wool may be used as petroleum hydrocarbons absorber during encapsulating process. The first purpose of the study was evaluation of petroleum hydrocarbons absorption by wool. The second aim of the work was to elaborate new method of wool entrapping into alginate capsules and checking of their absorption properties.

MATERIALS AND METHOD

Sodium Alginate – Manugel DJX (ISP, USA) was used for alginate/Ca beads preparation.
Sheep wool was used as hydrocarbons absorber
Petroleum hydrocarbons: diesel oil (Shell) and engine classic oil SJ/CF 15W/40 (ORLEN).
Hydrocarbons absorption by wool
a) 20g of engine oil have been put into 4 beakers and 20g of diesel oil have been put into 4 beakers. 0,5g piece, 1g piece, 1,5g piece and 2g piece of wool have been put into beakers with engine oil; the same pieces of wool have been put into beakers with diesel oil. After 24 hours of contact, the wool was taken of the beakers and weighted.
b) 20g of engine oil have been put into 4 beakers with 500ml of water, and 50g of diesel oil have been put into 4 beakers with 500ml of water. 5g piece and 10g piece of wool have been put into 2 beakers with engine oil and mixed using magnetic stirrer (Heidolph) with 300rpm. the same pieces of wool have been put into 2 beakers with diesel oil. After 24 hours of contact, the wool was taken of the beakers and weighted.

Capsule formation
a) 0,5g, 1g or 1,5g of wool have been put into beakers with an 1,5-2% aqueous solution of sodium alginate (in total 200 ml of solution) and mixed using magnetic stirrer (Heidolph) with 500rpm. In this method 50ml of alginate-wool mixture has been extruded as droplets using the disposable syringe into 0,155M solution of $CaCl_2$. After 20 minutes of reactions all capsules have been washed with water. All capsules have been prepared at room temperature.
b) 2g of wool has been cut into 0,02g - small fragments. Each fragment has been changed into globule. All 100 globules have been immersed separately into 1,5% aqueous solution of sodium alginate (in total 40 ml of solution); then the globules have been introduced one by one into 0,155M solution of $CaCl_2$. After 20 minutes of reactions all beads have been washed with water.
To determine the effectiveness of oils absorption by the beads that were obtained using both of method (method „A" and method „B"), 1g of capsules was introduced into diesel oil and into engine oil for 24 hours. After one day period of contact, the beads were taken of and weighted.
Mechanical characteristic of capsules
The quality of beads after 24h of contact with engine oil, diesel oil and also with water (Mediterranian and Baltic Sea salinity) was measured. The bursting force was indicated (using Zwick/Roell Z certified by ISO 5893 norm) to determine the quality of the beads. The bursting force of new prepared capsules (without contact with water and oils) was also measured as base value.

RESULTS AND DISCUSSION

Preliminary experiments showed that 0,5g of wool may absorb 11,2g of engine oil and 8,8g of diesel oil after 24 hours of contact. 1g pieces of wool may absorb only 18g of engine oil and 17g of diesel oil. It is important that 2g pieces of wool may absorb all 20g of analyzed oils; besides there was observed, that there were dry areas of wool on these pieces (Table 1).
Trials of capsulation by using of method „A" showed negative results. There was no possibility to mix 2% sodium alginate solution with wool fibres even the content of wool was lower than 0,25%. There was also no possibility to mix 1,5% sodium alginate solution with wool if content of wool was higher than 0,5%. Moreover the shape of capsules which were obtained by extruding wool-alginate mixture into calcium chloride solution by using syringe was not globular. The „capsules" which were obtained using method „A" were oval ended with short line. This shape was probably caused by wool fibres (Fig.1).

Mass of wool [g]	Absorption of oil [g / 1g of wool]	
	Engine oil	Diesel oil
0,5	22,4	17,6
1	18	17
1,5	12,6	12,5
2	10*	10*

Table 1: Absorption of engine/diesel oil by wool
*dry areas was observed even after 24 hours

Figure 1: Figure 1: Shape of „capsules" obtained using method „A"

Absorption of petroleum hydrocarbons by „capsules" prepared using method „A" was measured.

Results of the experiments showed, that ,,capsules" don't absorb engine and diesel oils. The reason is probably too low content of wool (0,25-0,5%) in these ,,capsules". Low oils absorption properties of ,,capsules" is the main cause that they should not be used in biodegradation process.
Shape of alginate capsules obtained using method ,,B" (approximately 10 mm in diameter) was globular (Fig 2). Mass of each capsule was 0,444g, thus the content of wool was 4,5%.

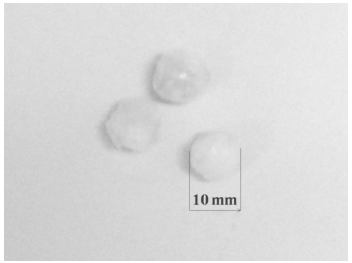

Figure 2: Shape of ,,capsules" obtained using method ,,B"

The effectiveness of oils absorption by capsules prepared using method ,,B" was evaluated. The results demonstrated that 21,2g of capsules (21,2g of capsules contains 1g of wool) may absorb about 0,33g of diesel oil and even 5,11g of engine oil (Table 2). The reason of this may be that absorption of engine oil is better than diesel oil and this is because engine oil contains hydrocarbons with hydrophilic groups. On the other hand, diesel oil as hydrophobic medium can be absorbed only by wool from calcium alginate capsules. It is necessary to say that these capsules may be suggested to be used in biodegradation process.

During bioremediation in marine environment, the capsules should be resistant to oils and also to salty water. That is the reason why bursting force of capsules after 24hours contact with oils and water with Mediterranean and Baltic Sea salinity was evaluated. The findings showed that bursting force of capsules decreased slightly from 14,97 N to 12,95 N (13,5%) and 12,88N (14%) after 24h of contact with analyzed oils. After one day of contact with distilled water bursting force also decreased a little. It is important to say that bursting force of capsules, which were incubated in water with Mediterranean and Baltic Sea salinity increased, but also narrowly (Table 3).

Petroleum hydrocarbons are major pollutants of marine environments as a result of terrestrial and fresh water run off, refuse from coastal oil refineries, shipping activities and accidental spills. The success of the application of a microbial inoculants depends on how favorable to its survival the target environments is or can be made [Gentili A.R. et al. 2006]. Immobilization of cells in polyurethane foam [Oh Y.S. et al. 2000, Patil N.K. et al. 2006, Quek E. et al. 2006] offers several advantages including high mechanical strength, resistant to organic solvents or cost effective, but also disadvantage for example: polyurethane foams are not biodegradable. The solution of this problem may be encapsulating. Naturally, so easy to degrade products as alginate are immobilizing carriers most frequently applied in natural systems [Bogusławska-Wąs E. et al. 2005]. Entrapping of microorganisms into alginate capsules is effective process. The problem is, that alginate capsules do not absorb hydrocarbons. In conclusion, wool entrapped into alginate capsules as petroleum hydrocarbons absorber may be effective method of new material formation from the viewpoint of its biodegradability and good absorption properties, also because of the stability in marine environment. The bursting force of alginate capsules with wool increases after 24 hours of contact

with sea water and it is a proof that mechanical properties of these capsules are good enough to use them in biodegradation process.

Content of wool in capsules [%]	Mass of oil [g / 1g of wool]	
	Diesel oil	Engine oil
4,5	0,33	5,11

Table 2: Absorption of engine/diesel oil by capsules obtained using method ,,B"

		Bursting force [N]
Capsules after preparing	Base value	14,97
Capsules after 24h of contact with:	Engine oil	12,95
	Diesel oil	12,88
	Water of Mediterranean Sea salinity	15,48
	Water of Baltic Sea salinity	16,09
	Distillated water	13,81

Table 3: Bursting force of the capsules obtained using method ,,b" after 24h of contact with oils and waters with different salinity

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